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Application of the Methods of Spin Chemistry to Establishment of the Nature of the Effect of Ordered Media on the Reactivity of Included Biologically Significant Compounds

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Abstract

An approach to the investigation of the effect of supramolecular structures on photoinduced radical processes is proposed. The possibilities of the new approach are demonstrated with the example describing the investigation of the effect of host–guest complexation of biologically significant photoactive molecules with β-cyclodextrin, both using the methods of spin chemistry and by means of laser flash photolysis. It was demonstrated that the effect of complexation affects the geminal processes and the processes taking place in volume with the participation of free radical species. Investigation of spin and molecular dynamics in these processes will allow one to establish the mechanisms of molecular recognition and the nature of selectivity in biological processes.

Key words: β-cyclodextrin, guest-host complexes, photo-CNP, laser flash photolysis

INTRODUCTION

The first notions concerning the possible effect of the so-called weak interactions, possessing much lower energy than the activation energy and chemical bond energy, on chemical processes were formulated by Professor V. V. Voevodsky in his works in early 1960es. One of the first confirmations of this prediction was the discovery of the magnetic effect in radical reactions [1]. Indeed, the energy of interaction of electron spins with the external magnetic field affecting the rate and direction of reactions is substantially lower than not only the energy of chemical bonds but also the thermal energy. The area that has been formed by present, namely spin chemistry, possesses a number of unique methods to investigate radical processes: chemical nuclear polarization (CNP), electron polarization (CEP), magnetic and magnetic isotope effects. The results of investigations of intimate mechanisms of these complicated processes with the help of these methods provide evidence that the weak interactions affect the course of chemical reaction. One of the examples of such an influence is the change of selectivity in radical reactions proceeding under the action of ordered media.

It is well known that the radical processes in homogeneous solutions are characterized by low selectivity, which is connected with the high reactivity of intermediates. The high activity of radicals in this case means that their recombination occurs with almost zero activation energy. Nevertheless, in reaction media different from homogeneous solutions, radical processes often exhibit high selectivity [2, 3]. This is especially typical for the processes occurring in animate nature. Enzymatic processes participated by coenzyme B_{12} for which the radical mechanism had been proven may be mentioned as an example [4]. It is believed that the selectivity of radical processes in biological systems is provided by enzyme-substrate complexes in which chemical transformations proceed. In this case, the dimensions of the active zone where the rupture or formation of a chemical bond of substrate molecule bound to the enzyme occurs are about 1 nm. It is necessary to stress that not every molecule can serve as a substrate for a specific enzyme. The criteria according to which an enzyme chooses a molecule for the formation of the enzyme-substrate complex are under extensive investigation and are known as the problems of molecular recognition [5].

The features determining the high selectivity of radical processes in biological systems and connected with the limitation of the reaction zone are characteristic also for some supramolecular structures: complexes of the host–guest type, micelles, zeolites. In this connection, the investigation of spin and molecular dynamics in radical reactions proceeding in supramolecular structures can help one to establish the mechanisms of molecular recognition and the nature of selectivity in biological processes.

By present, the effect of supramolecular structures on the selectivity of radical reactions was established for unimolecular photoinitiated processes as example [2, 3]. In this situation, changes in selectivity are observed both in the solid state and in solutions where the formation of supramolecular structures may be considered as a model of enzyme-substrate complexes. In essence, this is another manifestation of V. V. Voevodsky's idea of weak interactions when weak noncovalent binding of a molecule with its surroundings controls the rupture or formation of a covalent (chemical) bond inside the reaction zone. One of the fundamental problems is registration of changes of some properties of chemical compounds included into supramolecular structures, in comparison with their properties in homogeneous solutions.

In the present work, we propose the approach developed by us to study the effect of supramolecular structures on photoinduced radical processes. Within the framework of this approach, we record quantitative changes in the reactivity of photoactive molecules depending on the degree of their binding in supramolecular structures. The possibilities of the proposed approach are demonstrated for the investigation of photoinduced processes both using the methods of spin chemistry (CNP) and with the help of more conventional flash photolysis.

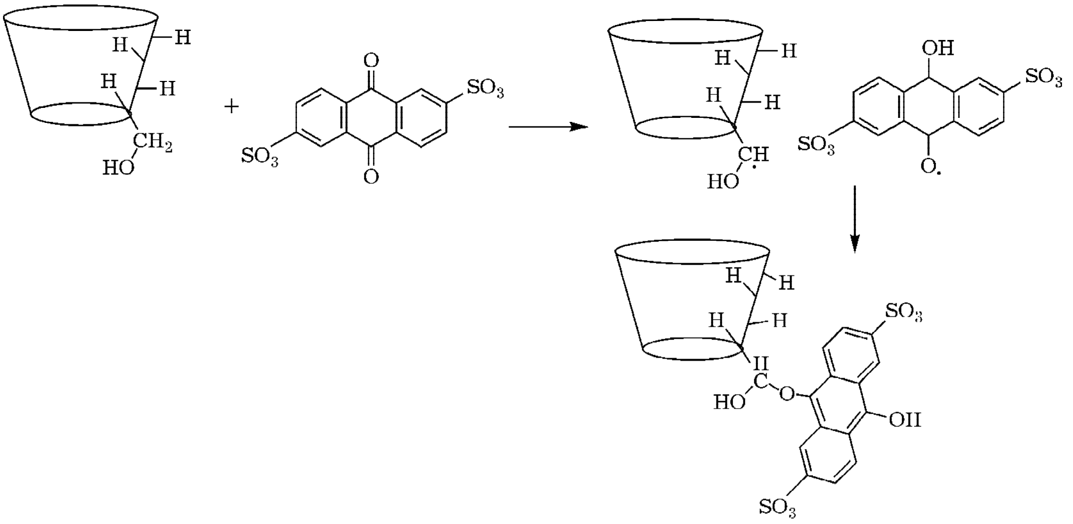
EXPERIMENTAL

The experimental procedure involving photo-CNP was described in detail elsewhere [6, 7]. Laser flash photolysis was carried out using the set-up at the Laboratory of Photochemistry of Institute of Chemical Kinetics and Combustion (ICKC), SB RAS (Novosibirsk). The sensitivity of the set-up with respect to optical density reached $5 \cdot 10^{-4}$, the spectral range was 300–750 nm [8]. The source of excitation radiation was a XeCl excimer laser with pulse duration ~15 ns and energy 30 mJ. β-Cyclodextrin (Aldrich Co.) was used without additional purification. dibenzylketone (Aldrich) was used after recrystallization from ethanol. Solutions were prepared using twice distilled water and methanol for UV spectroscopy. The volume fraction of methanol in aqueous solutions for photolysis was 5 %. The concentration of dibenzylketone was 0.5 mmol/L in all the experiments, the concentration of cyclodextrin was varied from 0 to 1 mmol/L. Higher cyclodextrin concentrations cause experimental complications due to the effect of light scattering by solutions on recording the intermediate absorption. With dibenzylketone concentrations used, the optical density at the wavelength of laser radiation was 0.1 and did not depend on the concentration of β-cyclodextrin. Irradiation was carried out in the spectrophotometric cell 1 cm high. To remove oxygen, the solutions were bubbled with argon for 15 min directly before irradiation.

RESULTS AND DISCUSSION

Previously we discovered selective photooxidation of CD molecule by the disodium salt of anthraquinone-2,6-disulphonic acid (AQDS) [6]. It was established on the basis of investigation of chemical nuclear polarization that oxidation proceeds according to the radical mechanism (Scheme 1).

It has also been established that AQDS forms an inclusion complex of host-guest type with CD. The constant of AQDS CD complex formation determined by means of NMR titration was (800±100) mol^{-1}. The structure of inclusion complex was determined with the help of 2D ROESY spectroscopy [9] and quantum chemical calculations (Fig. 1).



Scheme 1.

The character of the discovered reaction and the selectivity of the process may be easily explained on the basis of the data on the structure of the inclusion complex of AQDS and CD in which the oxygen atoms of AQDS are near the protons of CH_2OH group in CD. The dependence of CNP intensity of the product of selective oxidation on the molar fraction of AQDS included in the complex with CD. The molar fraction of AQDS in the complex was determined for the concentrations involved in the experiments using the constant of complex formation. The observed intensity of photo-CNP of the product of geminal recombination is determined as [10]

$$I_{\text{CNP}} = [\text{RP}]\Delta n_1$$

where [RP] is the concentration of geminal radical pairs; Δn_1 is the nonequilibrium difference of populations of the nuclear spin states formed during the geminal recombination of the radical pair. So, the intensity of polarization changes proportionally to the concentration of primary radical pairs.

One can see in Fig. 2 that the dependence of CNP intensity on the molar fraction of AQDS in the complex is well approximated with a linear dependence passing through the zero point. This is an evidence that the efficiency of the process under investigation is completely determined by complexing (the reaction occurs only in complex), while its selectivity is determined by the structure of the complex.

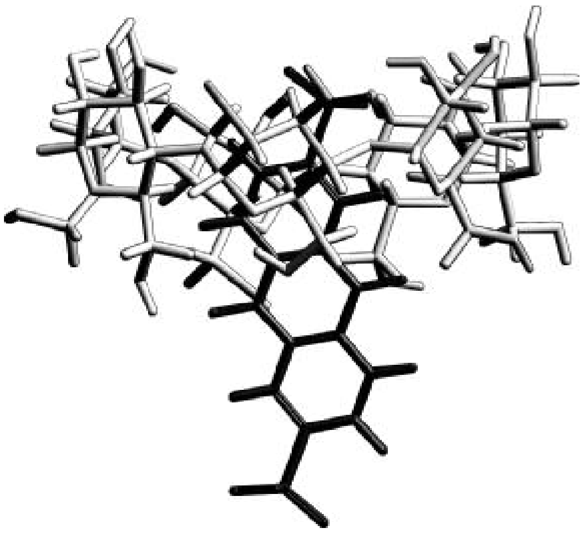


Fig. 1. Structure of inclusion complex of AQDS and CD.

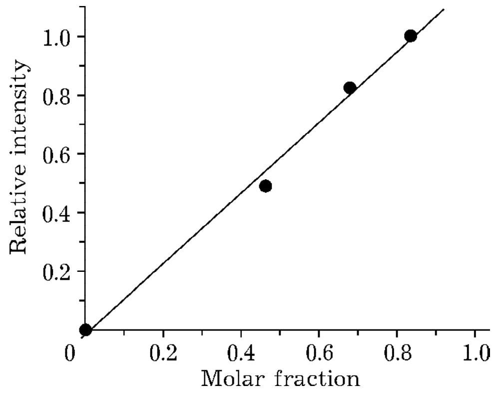
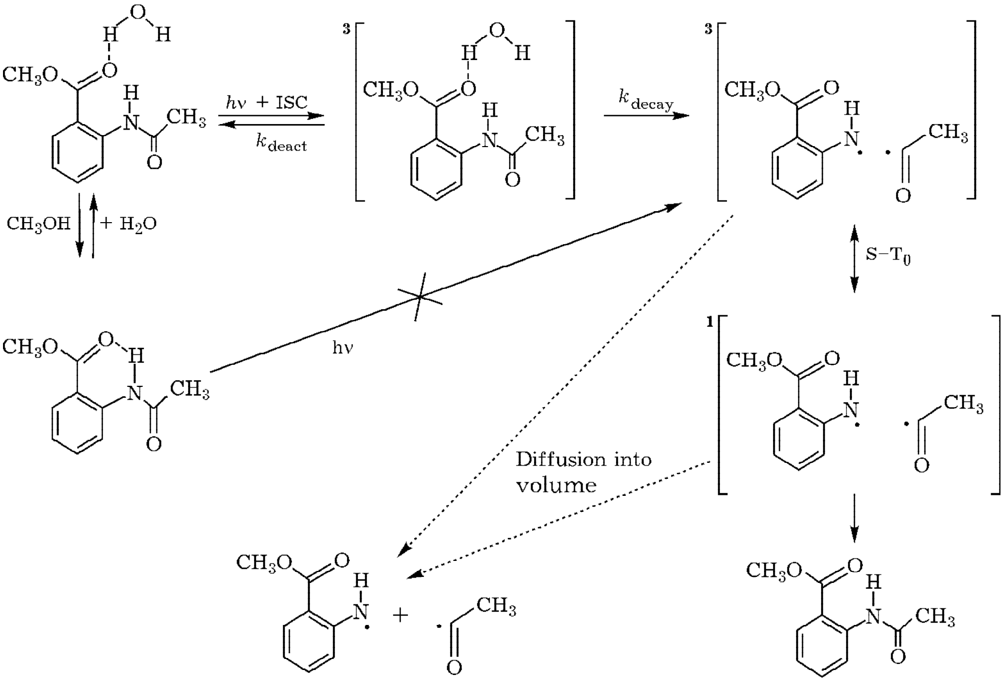


Fig. 2. Dependence of relative intensity of ^1H photo-CNP of the product of selective oxidation of CD on the molar fraction of AQDS in complex with CD [7].

Another example illustrating the productivity of the proposed approach is photodecomposition of the methyl ester of N-acylanthranilic acid (MA3) [7]. It was established previously that only those ester molecules in which the intramolecular hydrogen bond between the amide proton and carbonyl oxygen is absent undergo photodecomposition [7]. So, the efficiency of photodecomposition was completely determined by the shift of equilibrium between the MA3 forms with intra- and intermolecular hydrogen bonds. The mechanism of primary photolysis is presented in Scheme 2 [11].

Within the framework of this mechanism, the transfer of MA3 molecule from water into hydrophobic surroundings should cause a shift of equilibrium to the structure with the intramolecular hydrogen bond and therefore to a decrease in the efficiency of photode-composition. The efficiency of photodecomposition, similarly to the previous example, was followed as the changes in the intensity of CNP on the initial MA3 which is formed as a result of recombination of the geminal radical pair. According to the NMR spectroscopic data, in the case of the simultaneous presence of MA3 and CD in the water-alcohol solution (80 % water), the formation of the inclusion complex of host–guest type occurs with the constant (130±15) mol^{-1}. For MA3 concentration equal to 1 mmol/L, and CD concentration within the range 0–10 mmol/L, the molar fraction of MA3 bound in the complex with CD varies from 0 to 0.55.

The dependence of MA3 CNP intensity on the molar fraction of MA3 molecules in the inclusion complex is shown in Fig. 3. One can see that with an increase in the molar fraction of MA3 molecules in complex with CD the integral intensity of CNP of the aromatic protons of MA3 remains practically unchanged. It was demonstrated previously (see Fig. 2) that if the reactivity of the guest molecule is completely determined by complexation, then a change of the fraction of molecules in the complex state should cause a corresponding change of the process efficiency. The absence of such a correlation in this case is the evidence that complexation itself does not determine changes of the reactivity of the guest molecule. Therefore, similarly to the above-described case of AQDS complex with CD, change of the reactivity of the guest molecule is also due to the structure of inclusion complex. Analysis of the data of NMR spectroscopy and molecular modelling showed that the formation of inclusion complex occurs so that the MA3 molecule is localized in the hydrophobic cavity of CD; the aromatic ring of the ester is inside



Scheme 2.

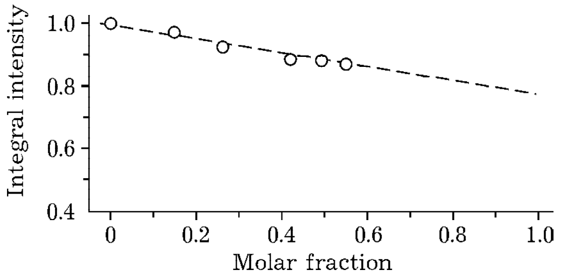


Fig. 3. Dependence of the integral intensity of CNP of H(5) aromatic protons on the molar fraction of free MA3 molecules [17].

the cavity, while the rest part of the molecule is outside the CD cavity [7] (Fig. 4). With such a structure of inclusion complex, water molecules have a free access tot eh carboxyl group, which according to the above-shown scheme does not lead to the shift of equilibrium to the form with the intramolecular hydrogen bond and thus to a decrease in the efficiency of photodecomposition. So, the efficiency of photodecomposition does not depend directly on the fraction of MA3 included into the complex.

Therefore, in the case when the intensity of polarization serves as a measure of the efficiency of photoinduced process, it is possible to establish the factors that are connected with complexation according to the host-guest type and define the reactivity of the photoactive guest molecules.

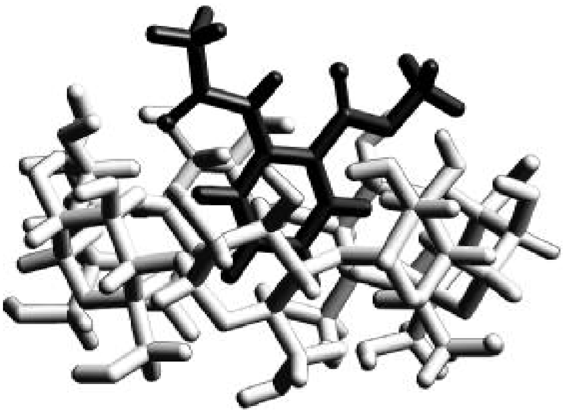
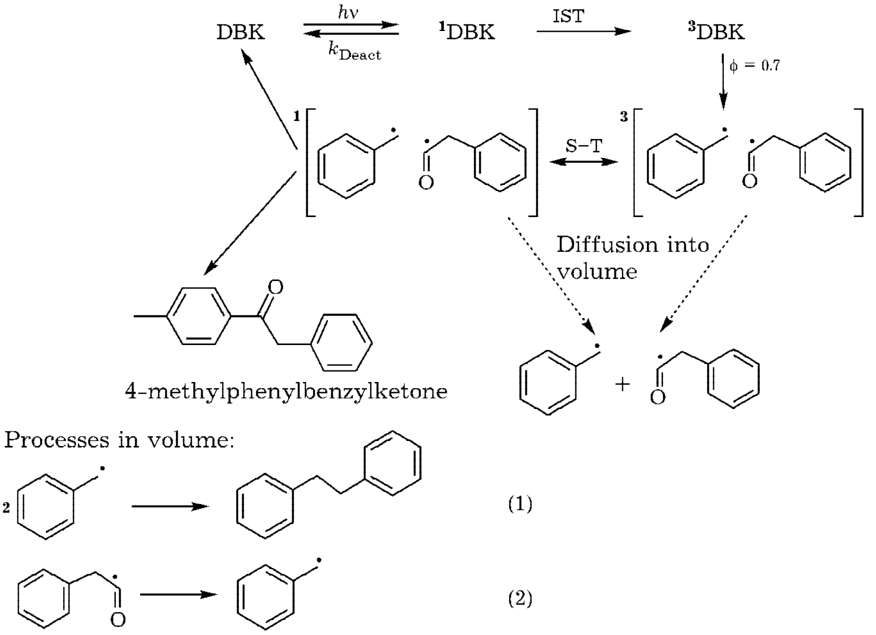


Fig. 4. Structure of the inclusion complex of MA3 and CD.

At the same time, the productivity of this approach has a general character and is independent of the experimental method used to investigate the reactivity. The correctness of this statement is confirmed by the results of the investigation of photolysis of dibenzylketone (DBK) using laser flash photolysis technique. The mechanism of DBK photolysis in a homogeneous medium had been studied using a variety of methods [12] and is presented in Scheme 3 in a general form.

According to Scheme 3, the reactive lower triplet state is formed as a result of intersystem crossing (ISC) from the lower excited singlet state in the picosecond time scale. The de-



Scheme 3.

cay of the triplet state leads tot eh formation of a radical pair of benzyl (Bz) and phenylacetyl radicals within several nanoseconds [12]. Geminal recombination also proceeds within several nanoseconds. The radicals that avoided geminal recombination are subject to further transformations. Decarbonylation of phenylacetyl radical in solution at room temperature occurs within several hundred nanoseconds and results in the formation of benzyl radical [13]. The quantum yield of photodissociation is ~0.7 [14]. Due to delocalization of the unpaired electron over the aromatic ring, benzyl radical is relatively stable. In this connection, in the majority of solvents including protonic ones, the role of the main channel of termination of benzyl radical is played by bimolecular recombination rather than the reaction with the solvent. Bimolecular recombination of benzyl radicals is practically a diffusion-controlled process. The steric factor of this process is equal to 0.8 [15], while the rate constant is ~10^8 mol^{-1}s^{-1} [16, 17]. Taking into account the above-mentioned data, the intermediate absorption in the laser flash photolysis experiment with submicrosecond resolution will be determined only by benzyl radicals.

Figure 5 shows the time dependencies of the intermediate absorption e for different CD concentrations at he wavelength of 316 nm, corresponding to $\varepsilon_{\max}$ of benzyl radical [18, 19]. It is known that the reaction of Bz termination in a homogeneous solution, for the time exceeding the time of decarbonylation of phenylacetyl radical, is well described by the second-order kinetics [20]. The dependence of reciprocal absorption on time (see insert in Fig. 5) shows that in the presence of CD, too, the temporal dependence of intermediate absorption for time >3 μs is also well described by the second-order kinetics. This is an evidence that the presence of cyclodextrin does not change the reaction order and the main channel of benzyl radical termination remains its bimolecular recombination with the formation of dibenzyl. A precise determination of the rate constant of recombination and the initial concentration of benzyl radicals is complicated due to essential scattering of literature data with respect to $\varepsilon_{\max}$ – from 1100 [21] to 12 000 [22]. Nevertheless, it was shown in [20] that the data on the ratio $k_2/\varepsilon_{\max}$ from different sources are in good agreement with each other. The value determined by simulation without CD $k_2/\varepsilon_{\max} = (1\pm0.1)\cdot10^5$ cm/s is also in good agreement with the literature data for the homogeneous solution with the viscosity of ~1 sentipoise ($1.2\cdot10^5$ cm/s).

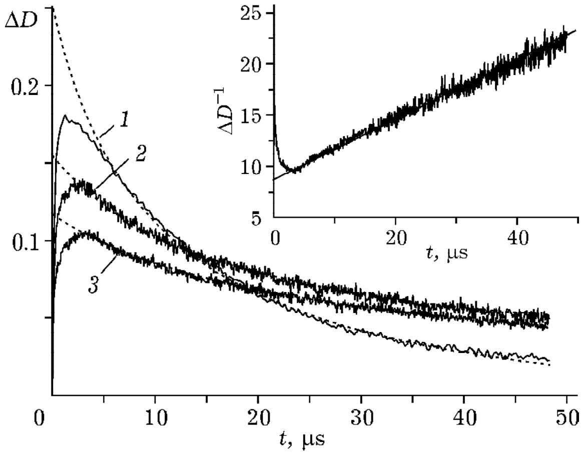


Fig. 5. Time dependencies of the intermediate absorption at 316 nm during the photolysis of water-methanol solution (5 % methanol) of 0.5 mmol/L DBK with different CD content, mol/L: 0 (*1*), 0.5 (*2*), 1 (*3*). Dotted lines correspond to simulation of the kinetics according to the second order; insert shows the dependence of reciprocal absorption on time for CD concentration 1 mmol/L.

It follows from the data shown in Fig. 5 that with an increase in CD content of solution the optical density ΔD_0 interpolated to zero time decrease, which corresponds to a decrease in the initial concentration of benzyl radicals with an increase in CD content. The latter may be connected with an increase in the probability of geminal recombination of the radical pair of benzyl and phenylacetyl radicals that are in complex with CD. In this case, the probability of geminal recombination of radical pairs that are formed during the photodecomposition of DBK molecule that is in complex with CD before it absorbs light is much higher than that for radical pairs formed from free DBK molecules in solution. Starting from this assumption, the initial concentration of benzyl radicals that avoided geminal recombination should correlate with the fraction of DBK molecules that are in complex with CD. The constant of DBK-CD complex formation is $1.16\cdot10^3$ mol^{-1} [23]; for concentrations involved in our work, this corresponds to a change of the molar fraction of DBK molecules in the free state from 0.53 to 1.

The dependence of interpolated optical density of benzyl radical (ΔD_0) on the molar fraction of DBK molecules in the free state is shown in Fig. 6. One can see that it is well approximated by a linear dependence passing through the zero point. This means that the intermediate absorption of benzyl radicals within the microsecond time scale is determined exclusively by the photolysis of DBK molecules in the free state. Such a behaviour of the system may be observed only in two cases: either DBK molecules in complex with CD do not undergo photolysis or the probability of geminal recombination in the complex is close to 1. According to literature data, the photolysis of DBK in complex does occur but the composition of products changes substantially in this case. For instance, the major product (with a 100 % yield) of the reaction in the case of photolysis in a homogeneous solution is represented by dibenzyl. In the case of photolysis of solutions with the high CD content, when the equilibrium is strongly shifted to the inclusion complex, the major product of reaction is 4-methyl-α-phenylacetophenon (yield: 81 %) [23]. It is necessary to stress that the formation of 4-methyl-α-phenylacetophenon is observed not only in the presence of CD but also in micellar solutions [24]. It was shown that it is formed in the recombination of the geminal pair through the attack of phenylacetyl radical at the *para*-position of the benzyl ring. Registration of the product of geminal recombination as the major product of photolysis is an evidence of the high probability of geminal recombination of the radical pair in complex with CD; this is in good agreement with the dependence of D_0 on the molar fraction of DBK in the free state observed by us. So, these data provide evidence that the intermediate absorption of benzyl radicals is determined only by photolysis of DBK molecules in the free state, while the photolysis of DBK in complex with CD does not lead to the escape of benzyl radicals into the volume due tot eh high probability of geminal recombination.

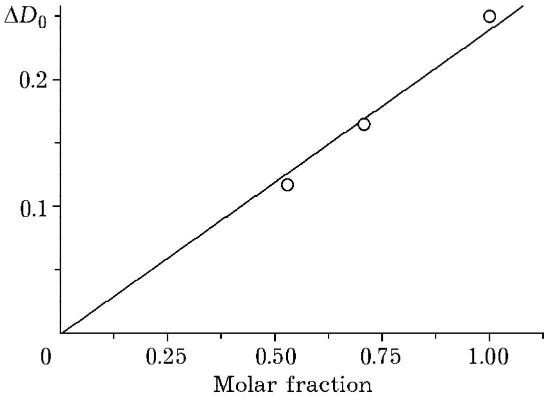


Fig. 6. Dependence of the optical density of benzyl radical interpolated to zero time (ΔD_0) on the molar fraction of DBK molecules in the free state.

Nevertheless, the effect of CD does not limited only to the effect on geminal recombination processes. The ratios of the rate constant of bimolecular recombination of benzyl radicals in solution to $\varepsilon_{\max}$ depending on the concentration of CD are listed in Table 1. One can see that with an increase in CD content in solution we observe a decrease in the effective recombination rate.

To establish the nature of the effect of CD on the processes in volume, let us consider possible processes with the participation of CD (Scheme 4).

With the above-listed $\varepsilon_{\max}$ values, the initial concentration of benzyl radicals in our experiments in the presence of CD may be $1 \cdot 10^{-5}$ to $1 \cdot 10^{-4}$ mol/L. The kinetics of the processes shown in Scheme 4 may be represented in the form

$$\frac{d[\mathrm{Bz}]}{dt} = -2k_1[\mathrm{Bz}]^2 - k_a[\mathrm{Bz}][\mathrm{CD}] + k_d[\mathrm{Bz:CD}] - k_2[\mathrm{Bz:CD}][\mathrm{Bz}] \quad (1)$$

$$\frac{d[\mathrm{Bz:CD}]}{dt} = k_a[\mathrm{Bz}][\mathrm{CD}] - k_d[\mathrm{Bz:CD}] - k_2[\mathrm{Bz:CD}][\mathrm{Bz}] - 2k_3[\mathrm{Bz:CD}]^2 \quad (2)$$

where k_1, k_2, k_a, k_d are the constants of the corresponding processes. The observed intermediate absorption is determined by the total concentration of free benzyl radicals and radicals in complex with CD. The kinetics of termination of benzyl radicals in all the forms is described as

$$\frac{d[\mathrm{Bz + Bz:CD}]}{dt} = -2k_1[\mathrm{Bz}]^2 - 2k_2[\mathrm{Bz:CD}][\mathrm{Bz}] - 2k_3[\mathrm{Bz:CD}]^2 \quad (3)$$

TABLE 1

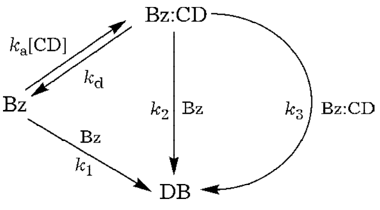
Ratio of the rate constant of bimolecular recombination of benzyl radicals (k) in solution to ε_{max} at different CD concentrations

CD concentration, mmol/L	[CD]/[DBK]	k/ε_{max}
0	0	$(10\pm1)\cdot10^4$
$5\cdot10^{-4}$	1	$(6\pm1)\cdot10^4$
$1\cdot10^{-3}$	2	$(4\pm1)\cdot10^4$

The process of formation of the complexes with CD is usually close to the diffusion control [25]. Therefore, for CD concentrations used in experiment, the equilibrium between the radicals in complex and in the free state is established rather rapidly being competitive with the process of bimolecular recombination (k_a[CD] > k_1[Bz]). Previously studying the photolysis of DBK in the presence of CD with the help of time-resolved CNP it was demonstrated that the benzyl radical in complex with CD is retained in the cavity of CD for more than 10 μs [26], which corresponds to the rate constant of complex dissociation $k_d < 10^5$ s^{-1}. If we assume that the formation of the complex of Bz with CD is close to diffusion control [25], the constant of complex formation $K_F = k_a/k_d > 10^3$. This value is close to the stability constant of the complex of CD with nitrophenol [27] which is similar to benzyl radical in size and structure. Within the framework of rather rapidly established equilibrium equation (3) may be represented as

$$\frac{d[\mathrm{Bz}+\mathrm{Bz}:\mathrm{CD}]}{dt} = -2\left\{\frac{k_1}{1+K_F[\mathrm{CD}]} + k_2 \frac{k_1}{K_F} + k_3(1+K_F[\mathrm{CD}])\right\}[\mathrm{Bz}+\mathrm{Bz}:\mathrm{CD}]^2 \qquad (4)$$

So, in the presence of CD the bimolecular character of benzyl radical termination is conserved with the effective rate constant depending on the concentration of CD and differing from the rate constant for the homogeneous solution. Taking into account the change of diffusion mobility of radicals in the free state and in complex, steric hindrance arising in complex during radical recombination, and our data obtained with the help of time-resolved photo-CNP [26], it is reasonable to assume that $k_1 > k_2 > k_3$. Within this assumption, one may provide an uncontradictory description of the observed changes of effective rate constant of bimolecular recombination of benzyl radicals in the presence of CD.



Scheme 4.

CONCLUSION

It is demonstrated that it is reasonable to use the developed approach in investigations of radical processes taking place in ordered media with the help of various experimental methods. It was established that the effect of complex formation is exhibited both in geminal processes and in the processes taking place in volume with the participation of radical species. In this situation, geminal processes are affected mainly by the structure of the complex with photoactive guest molecule through changes of the probability of geminal recombination. In volume processes, the effect is due to changes of radical lifetimes.

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